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Accelerated Testing Validation

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Project Start Date: Oct 2009
Project End Date: Sept 2014

Overall Objectives
- Correlation of the component lifetimes measured in an AST to "real-world" behavior of that component
- Validation of existing component specific ASTs for electrocatalysts, catalyst supports and membranes (mechanical and chemical degradation)
- Development of new ASTs for GDLs and bipolar plates
- Co-ordinate effort with Fuel Cell Tech Team and Durability Working Group

Fiscal Year (FY) 2014 Objectives
- Compare the US Drive new AST for carbon corrosion (1 to 1.5V cycle) with the US Drive old AST for carbon corrosion (1.2V hold)
- Development of a new Membrane AST that is representative of membrane degradation observed in the field and during the US Drive "Protocol for determining Cell/Stack durability"
- Development and validation of new AST for GDL materials

Technical Barriers
This project addresses the following technical barriers from section 3.4.5 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:
   (A) Durability
   (B) Cost

Technical Targets
Cost and durability are the major challenges to fuel cell commercialization. Accelerated Stress Tests (ASTs) enable rapid screening of fuel cell materials and are critical in meeting the long life times required for stationary and automotive environments. Moreover these

ASTs can also help predict the lifetime of the various components in "real-world" applications.

- Transportation Durability: 5,000 hours (with cycling)
    - Estimated start/stop cycles: 17,000
    - Estimated Frozen cycles: 1650
    - Estimated Load cycles: 1,200,000
    - Cost (30 $/kWe)
- Stationary Durability: 40,000 hours (2015); 60,000 hours (2020)
    - Survivability: Stationary -35 $^{\circ}$C to 40 $^{\circ}$C
- Bus Durability: 12 years/500,000 miles (2016 and ultimate)
    - Power plant lifetime: 18,000 hours (2016), 25,000 hours (ultimate)
    - Power plant cost: $450,000 (2016), $200,000 (ultimate)
    - Range: 300 miles; Fuel Economy: 8 miles/gallon diesel equivalent

FY 2014 Accomplishments

- Completed the US Drive 1 to 1.5V cycling AST on MEAs utilizing three different carbon types.
- Determined that the 1 to 1.5V cycling results in 1 order of magnitude greater carbon corrosion than the 1.2V hold
- Determined that the 1 to 1.5V cycling results in approximately 100 times faster Pt growth rate and voltage decay rate than the 1.2V hold
- The 1 to 1.5V cycling has the ability to clearly distinguish various carbon types with different degrees of graphitization
- Initiated development of a new membrane AST that has the ability to reproduce degradation mechanisms observed in the field and during simulated durability tests using the US Drive "Protocol for determining Cell/Stack durability"
- Developed a GDL degradation AST that results in similar degradation to that observed during durability tests using the US Drive "Protocol for determining Cell/Stack durability"
- GDL fingerprinting utilized to quantify GDL degradation

Introduction

The durability of polymer electrolyte membrane (PEM) fuel cells is a major barrier to the commercialization of these systems for stationary and transportation power applications.[1] Commercial viability depends on improving the durability of fuel cell components to increase the system reliability and to reduce system lifetime costs by reducing the stack replacement frequency. The need for Accelerated Stress Tests (ASTs) can be quickly understood given the target lives for fuel cell systems: 5000 hours (~ 7 months) for automotive, and 40,000 hrs (~ 4.6 years) for stationary systems. Thus testing methods that enable more rapid screening of individual components to determine their durability characteristics, such as off-line environmental testing, are needed for evaluating new component durability with a rapid turn-around time. This allows proposed improvements in a component to be evaluated rapidly and independently, subsequently allowing rapid advancement in PEM fuel cell durability. These tests are also crucial to developers in order to verify that durability is not sacrificed while making improvements in costs (e.g. lower platinum group metal [PGM] loading) and performance (e.g. thinner membrane or a GDL with better water management properties).

DOE has suggested AST protocols for use in evaluating materials, but only for the catalyst layer components (electrocatalyst and support), and for the membrane.[2,3] The US Fuel Cell Council (USFCC) has also suggested AST protocols for the same materials.[4] While these protocols have

concentrated on the catalyst, catalyst support and membrane materials, to date, no accelerated degradation protocols have been suggested for GDL materials or MPL layers, bipolar plates or seals. In spite of recent advances in AST development, a main portion, which is deficient, is the quantitative correlation between the results of a given fuel cell AST, and the degradation rate or life in an operating fuel cell.

Approach

A main desired outcome of this project is the correlation of the component lifetimes measured in an AST to *in situ* behavior of that component in "real-world" situations. This requires testing of components via ASTs and in operating fuel cells, and delineating the various component contributions to the overall cell degradation. This will primarily be performed by using a simplified 1-D model that takes into account the different component contributions like membrane ionic conductivity, cathode catalyst layer kinetic losses and mass transport losses (catalyst layer and GDL) to the overall losses observed in operating cells.[5] This project will then attempt to correlate the performance losses observed due to a particular component in "Real-world" situations with the degradation in AST metrics of that component. The correlation between AST and life data if State Of the Art (SOA) materials are used, in essence, gives one data point. Thus, for a reasonable correlation to be made, materials with different life spans are utilized in this project. The "real world" data utilized in this project include field data from Bus Fleets provided by Ballard Power Systems and simulated drive cycle data obtained at LANL utilizing the US Drive "Protocol for determining Cell/Stack durability"[6]. This work is also being coordinated with other funded projects examining durability through a DOE Durability Working Group.

Results

The US Drive Fuel Cell Technical Team (FCTT) recommended ASTs and protocol for determining cell/stack durability[6] was performed on various MEA/GDLs using $50cm^2$ single or quad-serpentine hardware purchased from Fuel Cell Technologies Inc. For carbon corrosion testing a California Analytical Instruments Inc. NDIR instrument was attached to the outlet N_2 from the cathode side (after condensing the water) to monitor total amount of CO_2 evolved. Polarization curves, ECSA, mass activity (MA), cross-over, shorting resistance and impedance measurements were performed at regular intervals to monitor the degradation rate.

Catalyst Degradation

The US Drive recommended 1 to 1.5V cycle was performed on MEAs utilizing 3 different carbon types, viz: E carbon (high surface area), V carbon (Vulcan) and EA carbon (graphitized low surface area). The NDIR analysis of the nitrogen at the cathode outlet clearly showed CO_2 corresponding to the corrosion of the carbon support in the cathode catalyst layer. Figure 1 a) illustrates the CO_2 evolved from the MEA using the EA-carbon support in the cathode catalyst layer. The CO_2 evolution steadily decreases over time as the number of cycles is increased. However, after characterization and resumption in testing an increased CO_2 evolution rate is observed. This is consistent with the formation of a passivation layer over time that can be reduced when the voltage is lowered below 1.0 V. NDIR results from the MEA utilizing the E-carbon (Fig. 1b) show that the corrosion rate from the high surface area carbon is almost an order of magnitude larger than the corrosion from the graphitized carbon. Moreover the E carbon also shows a dramatic lowering in the CO_2 evolution rate after 500 cycles consistent with the low amount of residual carbon in the catalyst layer (decreased catalyst layer thickness). This is also confirmed by large increases in mass transport losses in the MEA associated with catalyst layer compaction and loss in porosity. Figure 1 b also shows a comparison of the CO_2 emission from

the 1.2V hold AST showing about an order of magnitude greater CO_2 emission from the 1 to 1.5V cycling.

The MEA performance degradation observed during the 1.2V hold and the 1 to 1.5V cycling is compared in Figure 2a. The performance degradation rate during the 1 to 1.5V cycling is at least 2 orders of magnitude greater ($\approx$ 150x) than the degradation rate during the 1.2V hold. For example the polarization curves for the MEA using the V-carbon are similar after 80 hours (200 hours) of 1.2V hold and 1000 cycles (2000 cycles) from 1.0 to 1.5V corresponding to a cycling time of 0.56 hours (1.11 hours). Similar behavior was also observed for the MEA with the E-carbon electrode where the performance after 32 hours and 96 hours of 1.2V hold are similar to performance after 500 and 1000 cycles from 1.0 to 1.5 V respectively. Figure 2 b shows the Pt particle size measured by XRD (post testing) after various times of either the 1.2V hold or 1 to 1.5 V cycling ASTs. The time of the 1 to 1.5V cycling has been multiplied by 100 times clearly showing the 100 times acceleration factor of Pt growth in the 1 to 1.5V AST. Both ASTs also show a lowering of the degradation rate with increasing time consistent with the lower growth rate of the larger Pt particles.[7]

Membrane Degradation

Membrane degradation (increase in membrane cross-over) could be observed during durability testing using the US Drive "Protocol for determining Cell/Stack durability". While un-stabilized (both chemically and mechanically) membranes failed in < 1000 hours of this drive cycle testing, stabilized membranes showed excellent durability. For example the DuPont XL® membrane after 3800 hours of this drive cycle showed only a 30% decrease in membrane thickness, but failed at the edges due to the absence of a sub-gasket. Figure 3 a) is a back scattered SEM micrograph of the DuPont XL® membrane after 3800 hours of durability testing showing thinning (originally 25 μm) on the cathode (bottom) side of the reinforcement. A stabilized membrane from another supplier also lasted > 2000 hours with no change in membrane thickness but the test was aborted due to test stand issues. Further testing with sub-gasketing of both these stabilized-membranes is under progress to evaluate their life-time during drive cycle testing and should be close to the required 5000 hour durability target. The testing of un-stabilized membranes revealed both chemical and mechanical degradation as evidenced by global thinning and local tearing respectively. All membranes tested under this drive cycle failed due to mechanical degradation either at the edges (for stabilized membranes) or at the inlets/outlets (for un-stabilized membranes).

The current membrane ASTs fail to capture this failure mode and therefore a new RH cycling test in H_2/Air was developed to accelerate/simulate this membrane failure mechanism. The H_2/Air RH cycling was performed initially at a cell temperature of 80 °C with dry gases for 2 minutes and super saturated gases (dewpoint = 90 °C) for 2 minutes and resulted in failure of un-stabilized membranes in less than 300 hours (< 5000 cycles). However stabilized membranes hardly showed any degradation under this testing with no thinning or increase in cross-over observed even after 20,000 cycles ($\approx$ 55 days). In order to further accelerate this test, the cell temperature was increased to 90 °C with 2 mins of dry and 2 mins of super-saturated (dewpoint = 92 °C) gases. The cross-over of various stabilized and un-stabilized membranes subjected to this test is presented in Figure 3 b. The N211 membrane failed this test within 33 hours (1000 cycles) and exhibited both global thinning (40% reduction in thickness) and local tearing (several pinholes/cracks in membrane). However the stabilized DuPont XL® membrane showed no global thinning even after 600 hours of this testing ($\approx$ 10000 cycles) and showed increased cross-over due to edge failure. Another stabilized membrane with a sub gasket also lasted > 20,000 cycles with little increase in cross-over, indicating that further acceleration is required in order to

evaluate state-of-the-art membranes. This AST is being refined further in order to increase chemical degradation with respect to mechanical degradation by decreasing the time during the wet part of the RH cycle.

GDL Degradation

Gas diffusion layer degradation has been observed during drive cycle testing of fuel cells and an ex situ AST for GDL durability was reported last year. The ex situ ageing of GDL's was achieved by submerging them in a boiling solution of 30 % hydrogen peroxide (H_2O_2) at 95 ^{o}C for prolonged intervals up to 15 hours (this protocol was first reported by SGL as their part of the DECODE project). This test resulted in qualitatively similar degradation to that observed during drive cycle testing, i.e. increase in mass transport resistance of MEAs using aged GDLs. This year we have developed tests to quantify this degradation both in terms of fuel cell performance and materials property changes in the GDL. Mercury intrusion porosimetry (MIP) was used to monitor the changing average pore diameter and porosity of the GDL as a function of ageing time (see Fig. 4 a). The decreasing porosity and average pore diameter can be used to quantify GDL degradation and are consistent with the observed mass transport increases in MEAs utilizing aged GDLs. A RH fingerprint test as first reported by D. L. Wood et al[8] was utilized to quantify the performance changes observed due to GDL ageing. The performance of an MEA utilizing fresh and aged GDLs was monitored at a fixed voltage (selected to yield a current density of ≈ 1.5 A/cm^2) while varying the inlet dew point of the anode and cathode gases. The cell temperature was kept constant at 80 ^{o}C while the inlet dew points of H_2/Air were increased at 5 ^{o}C intervals from 30 ^{o}C to 80 ^{o}C. The performance of MEAs using fresh and 7 hours aged GDLs during this test is illustrated in Fig 4b). While the fresh GDL shows increasing performance with increasing RH, the aged GDL shows improved performance at low inlet RHs and a loss in performance at high inlet RHs. These results are consistent with improved HFR and better membrane hydration with the aged GDLs and improved mass transport with the fresh GDLs. The contact angles measured as a function of ageing time at 95 ^{o}C and 80 ^{o}C are plotted in Fig 4c and illustrate the increasing hydrophilicity of the GDL with ageing. The oxidation of the carbon in the GDL material results in the formation of hydrophilic surface oxide groups which in turn result in improved performance under drier conditions (improved membrane HFR) and degraded performance under wetter conditions (increased mass transport resistance). These tests will be utilized to quantitatively correlate in situ GDL degradation in MEAs with ex situ AST degradation of GDLs.

Conclusions and Future Directions

The electro-catalyst AST (0.6V to 1.0V cycling) was found to accurately capture the Pt ECSA loss occurring during wet/dry drive cycle testing. However this test needs further acceleration that can be achieved by increasing the voltage ramp rate. The US Drive recommended new AST (1.0 to 1.5V cycling) for carbon corrosion results in ten times greater carbon corrosion than the older 1.2V hold AST. The new AST results in ≈ 100 times acceleration of the Pt growth rate and the observed voltage decay rate. A new H_2/Air RH cycling AST which better simulates membrane degradation observed in the field and during drive cycle operation was developed. However, this AST requires further acceleration of chemical degradation with respect to mechanical degradation which will be achieved by decreasing the duration of the wet portion of the RH cycle with respect to the dry portion. Ex situ GDL ageing in peroxide solutions was found to degrade GDLs similar to those observed during drive cycle operation. GDL fingerprint test was found to be effective in characterizing GDL degradation and will be utilized to refine the GDL AST and to define accelerating factors with respect to drive cycle testing.

- AST testing
  - Further accelerate the catalyst cycling AST by speeding up the cycling rates from the current 50 mV/s. Perform an AST using a trapezoid wave with 0.5s rise time from 0.6V to 0.95V, 2.5s hold at 0.95V, 0.5s from 0.95 to 0.6V, and 2.5s hold at 0.6V
  - Refine membrane AST to better simulate membrane degradation observed during durability testing using the US Drive "Protocol for determining Cell/Stack durability"
- "Real-World" Testing
  - Perform simulated start/stop tests on MEAs utilizing 3 different carbon types
  - Perform the US Drive "Protocol for determining Cell/Stack durability" on MEAs using different membrane and catalyst layer types
- Characterization of materials
  - Perform *ex situ* characterization of catalyst particle size distribution, layer thickness, membrane thickness, and GDL hydrophobicity as a function of drive cycle and/or AST test time
- Correlation of AST to "Real-world" data
  - Determine acceleration factors of the membrane AST with respect to the US Drive "Protocol for determining Cell/Stack durability"
  - Determine acceleration factors of the 1 to 1.5V cycling AST with respect to the simulated start/stop cycles

FY 2013 Publications/Presentations

- •R. Mukundan, J. R. Davey, K. Rau, D. A. Langlois, D. Spernjak, J. D. Fairweather, K. Artyushkova, R. Schweiss, and R. L. Borup, "Degradation of Gas Diffusion Layers in PEM fuel cells during drive cycle operation," *ECS Transactions,* **V58(1)**, pp. 919-926 (2013).
- •M. P. Rodgers, L. J. Bonville, R. Mukundan, R. L. Borup, R. Ahluwalia, P. Beattie, R. P. Brooker, N. Mohajeri, H R. Kunz, D. K Slattery, and J. M Fenton, "Perfluorinated Sulfonic Acid Membrane and Membrane Electrode Assembly Degradation Correlating Accelerated Stress Testing and Lifetime Testing," *ECS Transactions,* **V58(1)**, pp. 129-148 (2013).
- •R. K. Ahluwalia, S. Arisetty, J.-K. Peng, R. Subbaraman, X. Wang, N. Kariuki, D. J Myers, R. Mukundan, R. Borup, and O. Polevaya, "Dynamics of Particle Growth and Electrochemical Surface Area Loss due to Platinum Dissolution," *Journal of The Electrochemical Society,* **V161**, pp. F291-F304 (2014).
- R. Mukundan, J. R. Davey, K. Rau, D. A. Langlois, D. Spernjak, J. D. Fairweather, K. Artyushkova, R. Schweiss, and R. L. Borup, "Degradation of Gas Diffusion Layers in PEM fuel cells during drive cycle operation," 224th Meeting of the Electrochemical Society, Oct 27-31, 2013
- M. P. Rodgers, L. J. Bonville, R. Mukundan, R. Borup, S. Knights, R. Ahluwalia,[e] P. Beattie, R. P. Brooker, N. Mohajeri, H. R. Kunz, D. K. Slattery, and J. M. Fenton, "The Chemistry of Membrane Degradation in PEM Fuel Cells" 225th Meeting of the Electrochemical Society, May 11-15, 2014 (Invited)
- R. Mukundan, P. Beattie, J. Davey, D. Langlois, D. Spernjak, J. Fairweather, D. Torraco, F. Garzon, A. Z Weber, K. More, and R. L. Borup, Durability of PEM fuel cells and the relevance of accelerated stress tests, 225th Meeting of the Electrochemical Society, May 11-15, 2014 (Invited)

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7. Z. Yang, S. Ball, D. Condit and M. Gummalla, J. Electrochem. Soc., **158(11)**, B1439-B1445 (2011).
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Acronyms

AST – Accelerated Stress Test
DOE – Department of Energy
DWG – Durability Working Group
ECSA – ElectroChemical Surface Area
GDL – Gas Diffusion Layer
HelOx – 21% Oxygen/79% Helium mixture
MA – Mass Activity
MEA – Membrane-Electrode-Assembly
MIP – Mercury Intrusion Porosimetry
MPL – Micro Porous Layer
MW-CNT – Multi walled carbon nano tube
NDIR – Non-Dispersive InfraRed
PEM – Polymer-Electrolyte-Membrane
RH – Relative Humidity
SEM – Scanning Electron Microscope
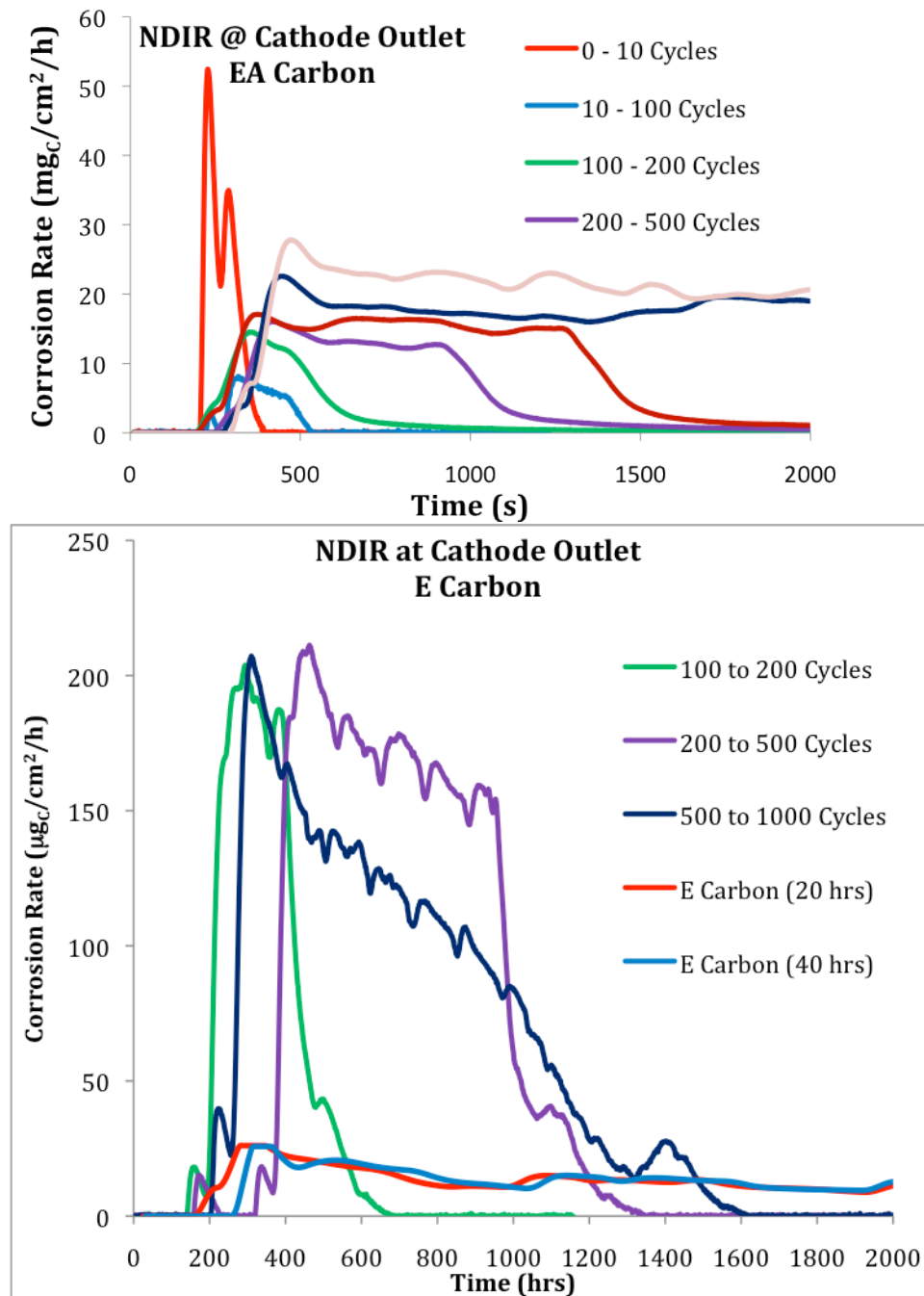USFCC – U.S. Fuel Cell Council

Figures

Figure 1. Carbon corrosion rate measured by the CO_2 concentration at the N_2 cathode (using an NDIR) during AST testing of MEAs utilizing Pt/C catalysts with a) low surface area graphitized carbon (EA-Carbon) and b) high surface area (E) carbon.
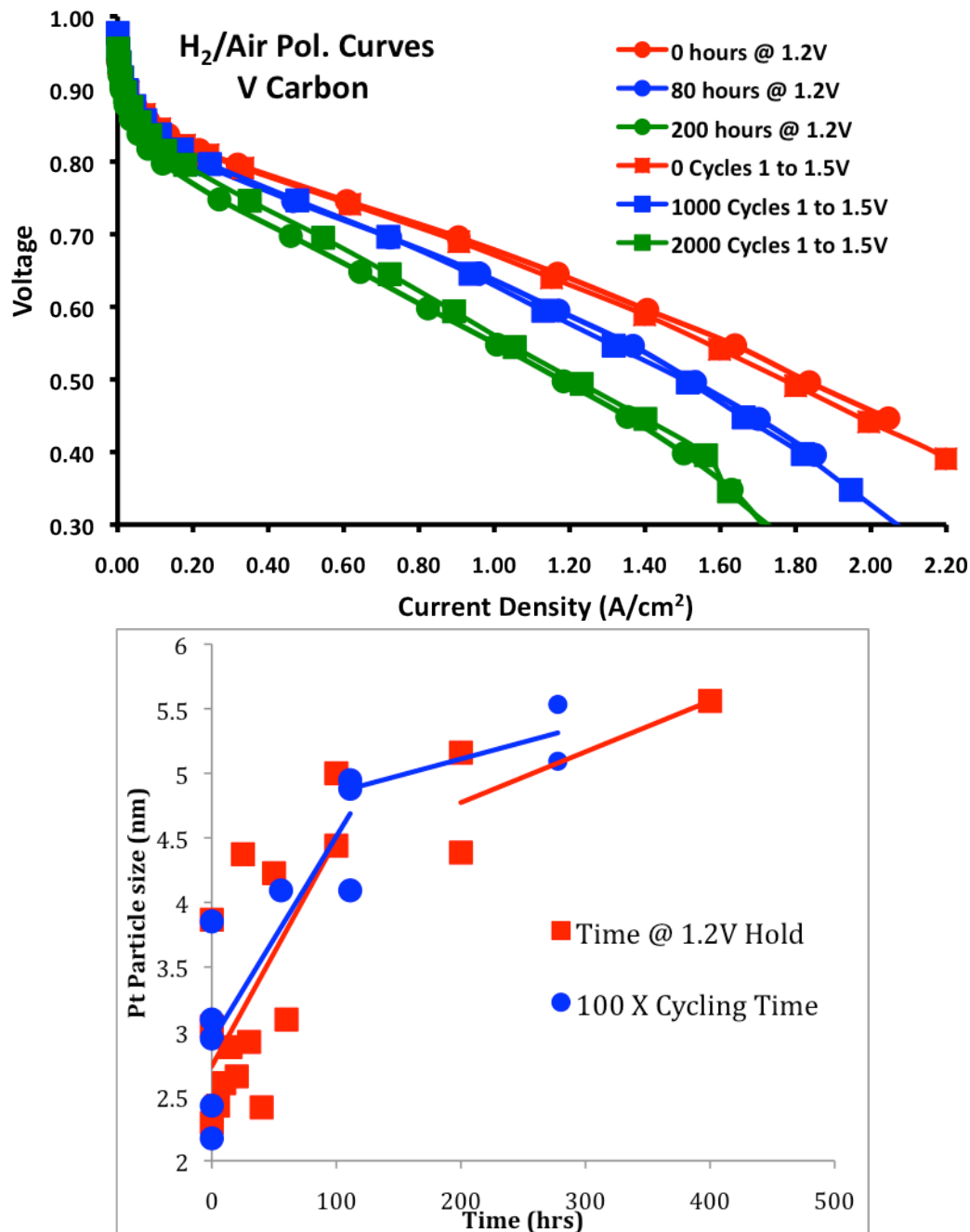
Figure 2. Comparison of a) Polarization curves measured after various times and b) Pt particle size evolution over time, during two different US Drive FCTT recommended carbon corrosion ASTs (1.2V hold and 1.0 to 1.5V cycling).
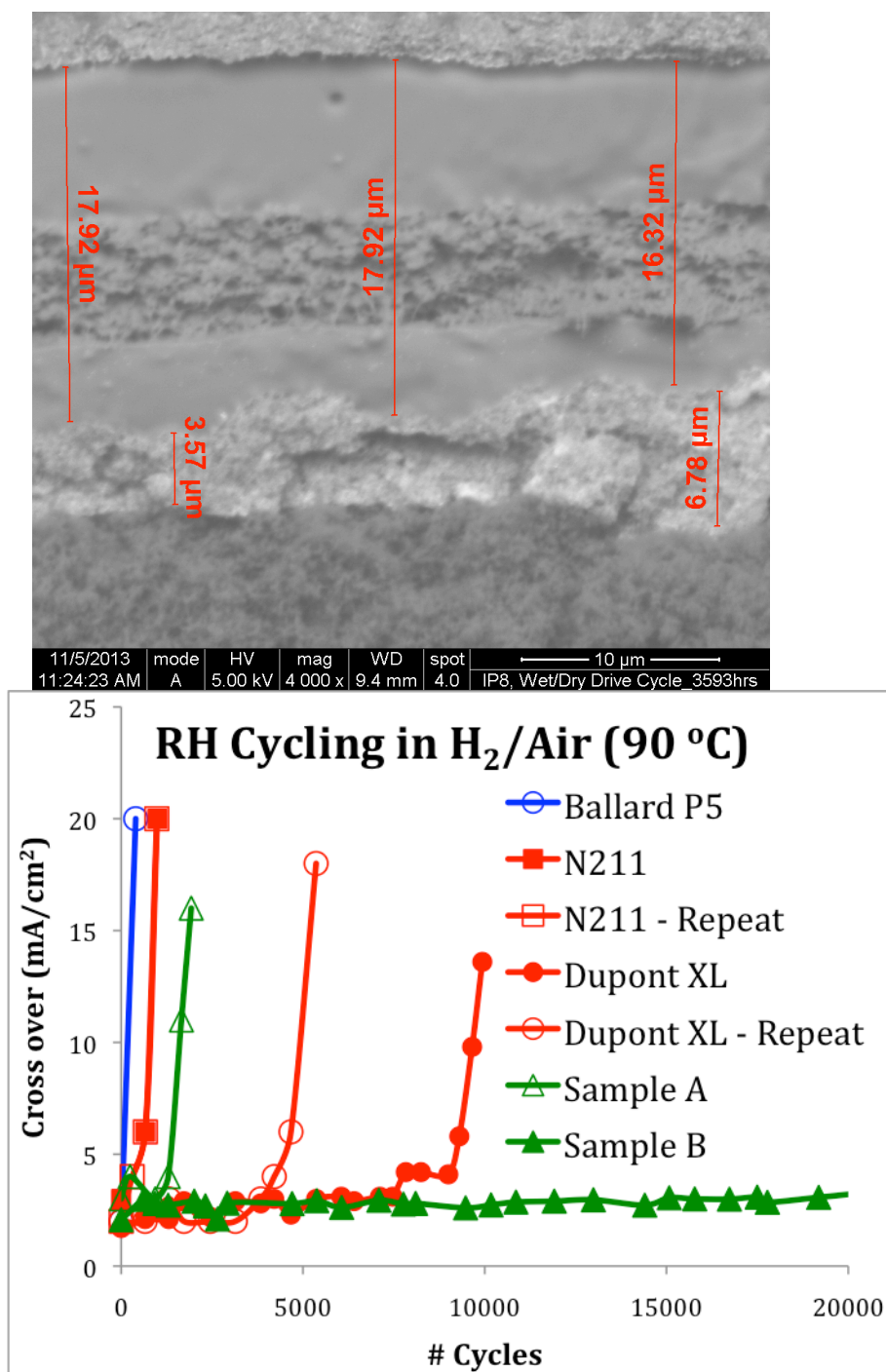
Figure 3. a) Backscattered SEM micrograph of DuPont XL® membrane after 3800 hours of drive cycle testing. b) Cross-over evolution of various membranes during RH cycling test in H_2/Air at a cell temperature of 90 °C.
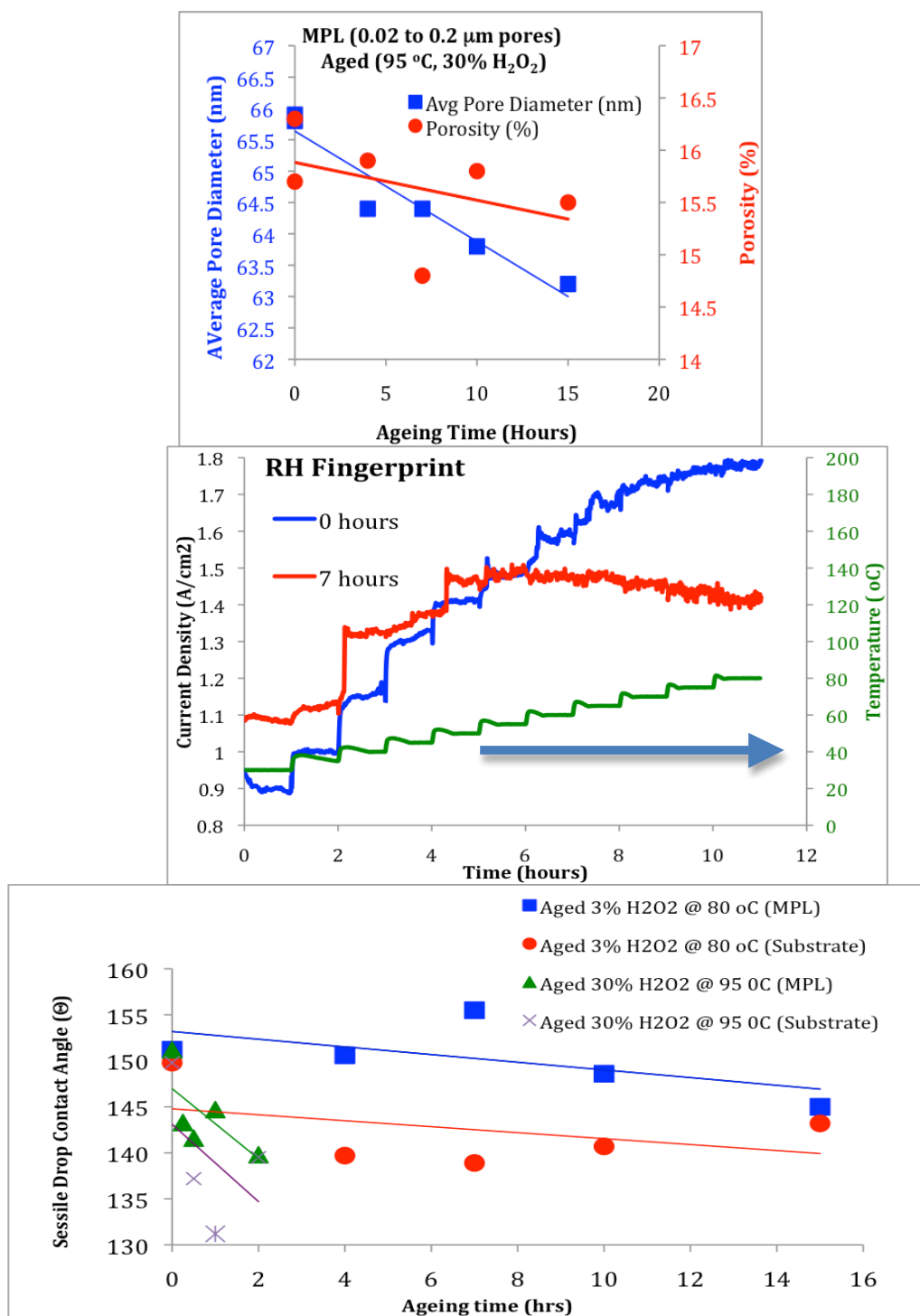
Figure 4. a) Decreasing porosity and average pore diameter of the GDL (measured using MIP) as a function of ageing time. b) GDL RH fingerprint: performance (current at 0.55V) of MEA as a function of cathode/anode inlet RHs of MEAs using fresh and 7-hour aged GDLs. c) Sessile drop contact angles of substrate and GDL as a function of AST ageing time.